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54 Catalyst for use in cleaning exhaust gas particulates.

57 Catalysts comprising in combination (a) metallic copper or a copper compound, (b) metallic molybdenum, metallic vanadium, a molybdenum compound or a vanadium compound, and (c) an alkali metal compound allow particulates in exhaust gases of Diesel engines to be burned at a relatively low temperature. For use, the catalyst is supported on a heat resistant particulate trap which is preferably coated with a carrier of titania, γ -alumina or silica-alumina, and then with the catalyst. Further enhanced catalytic activity is obtained when catalysts comprising components (a), (b), and (c) are combined with (d) metallic platinum, palladium or rhodium or its compound.

EP 0 092 023 A1

BACKGROUND OF THE INVENTION1. Field of the Invention

This invention relates to a novel and improved catalyst for use in cleaning particulates in exhaust gases, typically diesel engine exhaust gases, and more particularly, to a novel and improved catalyst with improved heat resistance which is carried on a particulate trap such that when particulate-containing exhaust gases are admitted into the particulate trap and the particulates are trapped by the particulate trap, the catalyst allows the trapped particulates to be burned at relatively low temperatures.

2. Prior Art

Recently, it became evident that particulates in exhaust gases, particularly particulates (minute particles of carbides such as soot) in diesel engine exhaust gases contain carcinogenic agents such as benzpyrene. Since such particulate-containing exhaust gases create a pollution problem, regulations on the emission of such exhaust gases are being scheduled.

To trap or collect such particulates, the prior art practice is to use heat-resistant traps including ceramic honeycombs, ceramic foams, ceramic fibers, metallic mesh loaded systems, and pellet carrier loaded systems (for example, alumina pellets). Although these traps can effectively trap or collect particulates, they tend to be clogged with accumulated particulates.

It is necessary to periodically remove accumulated particulates by disposal or combustion at elevated temperatures.

5 The disposal of accumulated particulates, which
may be carried out by blowing or washing, is trouble-
some to carry out and difficult to fully remove the
accumulated particulates, and will create secondary
pollution. The combustion of accumulated particulates
may be carried out by means of a burner, but requires
10 an elevated temperature as high as 700°C. In addition,
combustion as such imparts an undesirable thermal shock
to the trap itself to promote the deterioration thereof.
An additional risk is the evolution of harmful gases
such as carbon monoxide due to incomplete combustion.
15 There is the need for a technique capable of effective-
ly burning particulates accumulated on a particulate
trap or cleaner at a relatively low temperature.

 This invention is directed to a novel and
improved catalyst which allows particulates on a trap
20 to be burned at a sufficiently low temperature to
provide no thermal shock to the trap itself.

 A number of catalysts, particularly those based
on precious metals such as platinum and palladium are
well known in the art for the conversion of gaseous
25 harmful substances such as NO_x , carbon monoxide and
hydrocarbons in gasoline engine exhaust gases into harm-
less substances through catalytic oxidation. Such

catalysts, however, act in a completely different way from the particulate cleaning catalysts according to the present invention. For example, the platinum catalyst which is known to be the best catalyst for
5 cleaning gasoline engine exhaust gases was found to fail in effectively burning particulates.

Though it is known that particulates in exhaust gases are largely composed of carbon, no catalyst has been found in the prior art which enables the effective
10 catalytic combustion of such carbon particulates in low temperature.

SUMMARY OF THE INVENTION

The present invention provides a novel and improved catalyst system which allows particulates on a
15 trap to be effectively burned at relatively low temperatures. According to a first aspect of the invention, the above and other objects are achievable by a catalyst comprising in combination, (a) at least one component selected from metallic copper and copper compounds, (b)
20 at least one component selected from metallic molybdenum, metallic vanadium, molybdenum compounds and vanadium compounds, and (c) at least one component selected from alkali metal compounds. According to a second aspect of the invention, the catalyst comprising the three com-
25 ponents (a), (b), and (c) is combined with at least one carrier selected from titania, gamma-alumina, and silica-alumina. According to a third aspect of the invention,

the catalyst comprising the foregoing three components (a), (b), and (c) further comprises (d) at least one component selected from metallic platinum, metallic palladium, metallic rhodium, platinum compounds, 5 palladium compounds, and rhodium compounds, the catalyst being in combination with or without a carrier selected from titania, gamma-alumina, and silica-alumina.

When supported on a particulate trap in the form of a ceramic foam or honeycomb structure, the 10 catalyst of the invention allows particulates trapped or accumulated on the trap to be efficiently burned at a given exhaust gas temperature. Therefore, by supplying the catalyst according to the present invention onto a particulate trap, the particulate trap which is 15 free of clogging and requires no regeneration procedure may be obtained as long as proper conditions are met. Even when clogging occurs, the frequency thereof is minimized. Less frequent clogging results in less frequent regeneration wherein accumulated particulates 20 are removed through combustion by heating with a burner or an electric heater, or by intentionally quickly raising the exhaust gas temperature, minimizing thermal shock to the trap and protecting the trap from failure for a long period of time.

25 The catalysts of the invention have the advantages of heat resistance and durability. For example, the catalysts are not deactivated and retain their

catalytic activity when the trap temperature rises up to 900°C with the storage of heat of combustion of particulates. Of course, repeated regeneration procedures have little influence on the activity of
5 the catalysts.

Another advantage of the catalysts of the invention is that the oxygen concentration of exhaust gases has a minimal influence on the combustion of particulates. More specifically, the exhaust gas
10 oxygen concentration is generally low, and is often as low as 5% or below. In such a case, the combustion of particulates requires a higher temperature than in oxygen rich conditions. Nevertheless, the catalysts of the invention can keep the particulate combustion
15 temperature relatively low even at a reduced oxygen concentration.

The catalysts of the invention are also advantageous in that harmful gas such as hydrocarbons, carbon monoxide and nitrogen oxides in exhaust gases
20 can be catalytically reduced in amount in addition that particulates are fully burned.

Since the catalysts of the invention use base metals, they are less costly with a full supply of such catalyst components.

25 The above and other objects, features and advantages of this invention will be more fully understood from the following description.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The components constituting the catalysts of the invention will be described in detail. Component (a) used herein is one or more selected from metallic copper and copper compounds. The copper compounds include oxides, nitrates, halides (chlorides, bromides, etc.), carboxylates, sulfates, sulfites, phosphates, and other salts of copper which may be either monovalent or divalent. Among these, preferred are chlorides, nitrates and oxides of copper.

Component (b) is at least one compound selected from metallic molybdenum, metallic vanadium, molybdenum compounds and vanadium compounds. The compounds include oxides, nitrates, halides, carboxylates, sulfites, phosphates, and double salts of molybdenum and vanadium. More detailedly, examples of the molybdenum compounds include molybdenum trioxide, molybdic acid, ammonium molybdate, molybdenum chloride, molybdenum sulfide, molybdenum oxalate, sodium molybdate, potassium molybdate, etc. Examples of the vanadium compounds include ammonium vanadate, vanadyl dichloride, vanadium oxytrichloride, vanadyl sulfate, vanadium pentoxide, vanadium trioxide, vanadium dichloride, vanadium trichloride, vanadium tetrachloride, lithium vanadate, sodium vanadate, potassium vanadate, and oxides and sintered products thereof.

Component (c) is an alkali metal compound.

More specifically, component (c) is at least one selected from compounds of lithium, sodium, potassium, rubidium and cesium. Various types of compounds may be used including oxides, nitrates, halides, carboxy-
5 lates, sulfites, nitrates and phosphates, with chlorides and nitrates being most preferred. Among the alkali metals, potassium, sodium and lithium are preferred, and chlorides thereof are most preferred. Potassium chloride is the best.

10 Also included are so-called double salts containing at least two metals of components (a), (b), and (c).

 The catalysts comprising components (a), (b), and (c) may be prepared in any desired manner, for
15 example, by mixing aqueous solutions of components (a), (b), and (c) in a suitable proportion and applying the mixed solution to a trap. Alternatively, solutions of the respective components in water or organic solvents such as alcohol may be separately or in
20 admixture of two, applied to a trap in sequence. Thermal spraying method is also applicable when the metallic components of (a) and/or (b) are used.

 It has been found that the activity of the catalyst of the invention is enhanced by further com-
25 bining it with at least one carrier selected from titania, gamma-alumina, and silica-alumina, with titania being most preferred. The combination of the catalyst

with these carriers results in an additional great advantage that the catalyst is further improved in heat resistance because, according to the inventors' assumption, the respective components of the catalyst
5 are spread over the surface of the carrier, that is titania, gamma-alumina or silica-alumina, to form an active steady catalyst surface. These carriers may be used in admixture with the components of the catalyst. Alternatively, a trap may be pre-coated
10 over its surface with any of these carriers before the components (a), (b), and (c) are simultaneously or separately applied to the trap. The carriers may further include those which form a double salt with one or more metals of components (a), (b), and (c), for
15 example, potassium titanate and sodium titanate. In this case, the catalyst metal contained in the carrier may be eliminated from the catalyst.

According to the present invention, catalysts comprising components (a), (b), and (c) with or with-
20 out a titania, gamma-alumina or silica-alumina carrier may be further enhanced in activity when they are combined with at least one component (d) selected from metallic platinum, metallic palladium, metallic rhodium, platinum compounds, palladium compounds, and
25 rhodium compounds. The compounds used as component (d) include oxides, halides, nitrates, carboxylates, phosphates, and other double salts, with halides being

preferred. Component (d) may be incorporated into the catalyst in any desired manner, for example, by applying it to a trap on which the components (a), (b), and (c) have been supported together with or without a carrier of titania or the like. Alternatively, component (d) may be applied to a trap in the same manner and at the same time as components (a), (b), and (c), that is, separately or in admixture with any component.

Component (d) is effective particularly when fuel or certain hydrocarbons are intentionally admitted into exhaust gases, or the engine is controlled such that hydrocarbons or carbon monoxide is entrained in the exhaust gases, because the catalyst containing component (d) allows such additives or contaminants to be burned at a further lower temperature and promotes the simultaneous combustion of particulates. The catalyst is also effective in removing harmful substances such as hydrocarbons and carbon monoxide in exhaust gases.

The above-mentioned catalyst components (a), (b), (c) and (d), and the carriers may be supported on a trap in an amount of 0.01 to 30% by weight, preferably 0.1 to 20% by weight of the trap, respectively.

The catalysts of the invention may be attached to a trap by a non-limiting method, usually by immersing the trap in a solution of the catalyst or each

component thereof, drying the immersed trap, and calcining the trap at a given temperature of 100°C to 900°C.

The trap used herein may be selected from
5 ceramic foams, ceramic honeycombs, ceramic fibers, ceramic particles, metal mesh, and the like. Among these, ceramic foams are preferred because of ease of attachment of the catalyst thereto and elimination of clogging. In general, those ceramic foams having
10 6 to 150 open cells per linear inch and a bulk specific gravity of 0.2 to 1.0 are preferred, though not limited thereto.

One ceramic foam of desired size may suffice the purpose though a plurality of ceramic foams may
15 be used in proper combination. For example, a plurality of ceramic foams may be arranged in series from the coarsest foam (having the largest interconnected cells) to the densest foam (having the smallest interconnected cells) in a side-by-side relation-
20 ship. Of course, the method of attaching the catalyst to the trap may be varied with particular requirements. The catalysts of the invention may advantageously be combined with any well-known catalyst.

The trap or cleaner on which the catalyst of
25 the invention is supported is placed in a flow path of exhaust gases from an engine or other source such that the exhaust gases will pass through flow channels in

the trap where particulates contained therein are effectively trapped or collected by the trap. The trapped particulates are completely burned at a temperature lower by 200°C to 300°C than in the absence of the catalyst of the invention.

The catalysts of the invention may be used for the removal of particulates in emissions from engines of transport vehicles such as ships and trains, agricultural machines such as combines, industrial engines, combustion furnaces and boilers as well as emissions from automobile engines.

In order to further illustrate the present invention, examples thereof will be shown together with comparative examples. However, the present invention is not limited to the below-mentioned examples.

Example 1 and Comparative Examples 1 - 3

A mixture of 1.5 mmol of copper chloride and 1.5 mmol of potassium chloride was dissolved in distilled water in a 10-ml beaker, a separately prepared solution of 0.73 mmol of ammonium molybdate in water was added to the solution, and 0.5 g of titania was added to the mixed solution. With stirring, the slurry was evaporated to dryness on a hot plate over a period of about 10 minutes. The resulting mass was dried for a further 120 minutes in a vacuum dryer at 200°C, and then calcined for 30 minutes in an electric furnace at 700°C. Another sample was prepared by repeating the

same procedure as above except that it was calcined at 900°C. Each of the catalyst samples was mixed with particulates previously collected from Diesel engine emissions at a weight ratio of 1:1. The combustion temperature of Diesel engine emission particulates was measured by a thermogravimetric analyzer at an air feed rate of 0.5 liters/min. and a temperature rise rate of 20°C/min. An intermediate combustion temperature, T_m (°C) was determined on the basis of the resulting thermogravimetric diagram. (It was separately affirmed that the T_m value is one measure for the evaluation of complete combustion of particulates.)

For the sake of comparison, using a binary system of copper chloride combined with potassium chloride, a single system of ammonium molybdate, and another single system of potassium chloride (total amount of catalyst component(s) 3.72 mmol and titania 0.5 g in either case), catalyst samples were similarly prepared. The particulate combustion temperature T_m was measured for each catalyst sample. The results are shown in Table 1.

Table 1

	Catalyst system	T _m (700°C calci- nation)	T _m (900°C calci- nation)
Example 1	Cu-K-Mo	347°C	364°C
Comparative Example 1	Cu-K	331°C	473°C
Comparative Example 2	Mo	469°C	552°C
Comparative Example 3	K	550°C	610°C

As apparent from the data of Table 1, the catalysts of the present invention, irrespective of whether they are calcined at 700°C or 900°C, are effective in reducing the combustion temperature.

Binary system catalysts as exemplified by Comparative Example 1 are fully active when calcined at 700°C, but are deactivated when calcined at 900°C. Single system catalysts as exemplified by Comparative Examples 2 and 3 only show less or little catalytic activity.

Examples 2 - 11

Catalysts were prepared from copper chloride-potassium chloride-ammonium molybdate and copper chloride-potassium chloride-ammonium vanadate systems by following the same procedure as in Example 1, and combined with titania, silica-alumina and gamma-alumina carriers, respectively. The combustion behavior of Diesel engine emission particulates was examined for

each catalyst sample under the same conditions as in Example 1. These catalyst samples were also combined with cordierite and magnesia which are commonly used to make ceramic foams or honeycombs, and subjected to the same test. It is to be noted that all the catalyst samples were calcined at a temperature of 900°C. The results are shown in Table 2.

Table 2

	Catalyst system	T _m (900°C calcination)
Example 2	Cu-K-Mo + titania	360°C
Example 3	" + silica-alumina	388°C
Example 4	" + γ-alumina	391°C
Example 5	" + cordierite	400°C
Example 6	" + magnesia	436°C
Example 7	Cu-K-V + titania	376°C
Example 8	" + silica-alumina	399°C
Example 9	" + γ-alumina	395°C
Example 10	" + cordierite	440°C
Example 11	" + magnesia	443°C

As seen from Table 2, catalyst systems according to the present invention based on three-component catalysts combined with titania, silica-alumina, and gamma-alumina carriers afford significant effect.

Examples 12 - 15

Three-component catalysts combined with titania (0.5 g) were prepared by the same procedure as in Example 1 except that copper nitrate, ammonium vanadate or ammonium molybdate, and lithium chloride or sodium chloride were used as the catalyst components, and then subjected to the same particulate combustion test as in Example 1. It is to be noted that all the catalyst samples were calcined at a temperature of 700°C for 30 minutes. The molar ratios of the catalyst components used and the results of the intermediate combustion temperature T_m of the catalyst systems are shown in Table 3.

Table 3

	Catalyst components (molar ratio)	T_m (700°C calcination)
Example 12	Cu:Mo:Li = 2:2:6	405°C
Example 13	Cu:V :Li = 4:2:4	379°C
Example 14	Cu:Mo:Na = 2:2:6	410°C
Example 15	Cu:V :Na = 4:2:4	390°C

As also seen from Table 3, it is evident that the particulate combustion temperature is substantially reduced by catalyst systems according to the present invention.

Example 16

A ceramic foam in the form of a 9.5-cm diameter, 10-cm long cylinder made of cordierite and having about 20 interconnected cells per linear inch was immersed in an aqueous solution containing 15% by weight of ammonium vanadate, lithium chloride and copper nitrate (molar ratio 2:6:2). The ceramic foam was taken out of the solution, centrifuged to remove excess solution, dried, and calcined in air at 700°C for 30 minutes.

The catalyzed ceramic foam was placed in an exhaust pipe at a distance of 1.5 meters from the exhaust port of a Diesel engine which was operated for 30 minutes at 900 r.p.m. and a torque of 8.9 kg-m. There were trapped 3.5 g of Diesel particulates. A cubic piece of about 2 x 2 x 2 cm was cut out of the central portion of the ceramic foam, and the particulate combustion temperature was measured to be 376°C by a thermogravimetric analyzer.

For the sake of comparison, a similar experiment was conducted on a non-catalyzed ceramic foam to find a particulate combustion temperature of 650°C.

It is evident that the vanadium-lithium-copper catalyst supported on a ceramic also has a great effect in reducing Diesel particulate combustion temperature.

Example 17 and Comparative Example 4

Catalysts were prepared and the combustion

behavior of Diesel engine emission particulates was examined by following the procedures of Example 1 except that the catalyst components used were 1.5 mmol of copper chloride, 0.73 mmol of ammonium molybdate, and 0.5 g of potassium titanate. For the sake of comparison, a similar experiment was carried out using the identical amounts of copper chloride and ammonium molybdate and 0.5 g of titania. The results are shown in Table 4.

Table 4

	Catalyst component	T _m (700°C calcination)
Example 17	$\text{CuCl}_2 \cdot (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot \text{K}_2\text{O} \cdot \text{TiO}_2$	369°C
Comparative Example 4	$\text{CuCl}_2 \cdot (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot \text{TiO}_2$	452°C

As seen from Table 4, the catalyst of Example 17 having potassium titanate incorporated shows catalytic activity comparable to that of the catalyst of Example 2 having KCl and titania incorporated. On the other hand, the alkali metal-free catalyst of Comparative Example 4 shows reduced catalytic activity.

Example 18

A ceramic foam in the form of a 9.5-cm diameter, 10-cm long cylinder made of cordierite and having about 30 interconnected cells per linear inch was immersed in

a slurry of titania, centrifuged to remove excess slurry, air dried, and calcined for 5 hours at a temperature of 500°C, resulting in a titania-coated ceramic foam. The amount of titania supported on
5 the foam was 5% by weight of the total weight of the coated ceramic foam. A catalyst consisting of copper chloride, ammonium molybdate and potassium chloride was applied to the coated ceramic foam, which was dried and then calcined for 30 minutes at
10 500°C. The molar ratio of Cu:Mo:K was 4:2:4.

The catalyzed ceramic foam was placed in an exhaust pipe at a distance of 1.5 meters from the exhaust port of a 1.8-liter Diesel engine which was operated at 3000 r.p.m. under a 67% load. The foam
15 was exposed to the exhaust gases having a temperature of 460°C and an oxygen concentration of 6.8%.

A similar experiment was repeated on a catalyst-free ceramic foam of the same configuration as a control.

20 It was found that the catalyst-free system experienced back pressure increases of 50 mmHg and 90 mmHg relative to the initial value after 30 minutes and 60 minutes runs, whereas the catalyzed system according to the present invention experienced back
25 pressure increases of 25 mmHg and 35 mmHg after the same runs, indicating a slowdown in back pressure rise. It was proved that the catalyzed system according

to the present invention allows particulates to be burned in the ceramic foam to prevent the rise of the back pressure.

Example 19

5 By following the procedure of Example 18, a ceramic foam having a Cu-Mo-K catalyst supported thereon was prepared. The catalyzed ceramic foam and a catalyst-free ceramic foam were examined for the dependency of particulate combustion behavior on
10 oxygen concentration. Each trap was placed in an exhaust pipe from a 1.8-liter Diesel engine which was operated under high soot emission conditions, that is, at 1,500 r.p.m. under a 80% load. The trap having a known amount of particulates deposited thereon was
15 connected to a hot air generator to examine the combustion of particulates at oxygen concentrations of 20% and 5%. It was found that the catalyst-free system showed initial and final combustion temperatures of 490°C and 620°C at an oxygen concentration of 20%, and
20 both the initial and final combustion temperatures were increased to 520°C and 700°C at an oxygen concentration of 5%. On the contrary, the catalyzed system shows initial/final combustion temperatures of 300°C/440°C and 320°C/460°C at oxygen concentrations of 20% and 5%,
25 respectively, and hence, shows no significant difference in combustion temperature between higher and lower oxygen concentrations, affording steady combustion

behavior at a relatively low temperature.

Example 20

By following the procedure of Example 18, a ceramic foam having a Cu-Mo-K catalyst supported thereon was prepared. The catalyzed ceramic foam and a catalyst-free ceramic foam were examined for particulate combustion behavior to measure the concentration of carbon monoxide in the resulting combustion gas. Each trap was connected to a 1.8-liter Diesel engine which was operated under high soot emission conditions, that is, at 1,500 r.p.m. under a 80% load, to thereby deposit particulates on the trap. Hot air at 490°C was passed through the trap having particulates deposited thereon, and the concentration of carbon monoxide in the gas emerging from the trap was measured by gas chromatography. The percentage of $\text{CO}/(\text{CO} + \text{CO}_2)$ was 47% for the catalyst-free trap, but was reduced to 16% for the catalyzed trap.

Example 21

A catalyst designated "catalyst A" was prepared by substantially the same procedure as in Example 1, that is, by using copper chloride, ammonium molybdate and potassium chloride in a molar ratio of 2:1:2 together with titania. Another catalyst designated "catalyst B" was prepared by dissolving 3.72 mmol of chloroplatinic acid in distilled water, mixing the solution with 0.5 g of gamma-alumina, evaporating the

slurry to dryness on a hot plate, vacuum drying the mass, and calcining the mass for 2 hours in an electric furnace at 450°C.

Catalyst A, catalyst B, and a mixture of them were mixed with soot emitted from a Diesel engine during normal mode operation, and were examined for combustion behavior. The results are shown in Table 5.

Table 5

Catalyst	T _m (°C)
B; Pt system	452
A; Cu-Mo-K system	325
A + B (weight ratio 10:1)	314

The additive effect due to catalyst B was recognized.

The same results were obtained by using palladium chloride or rhodium chloride instead of chloroplatinic acid.

Furthermore, it was examined how the mixture of catalyst A and catalyst B was effective in reducing CO in exhaust gas. The amounts of CO₂ and CO in exhaust gas at 150°C were measured by gas chromatography before and after its contact with the catalyst mixture. The ratio CO/(CO + CO₂) was reduced to about 6 after the catalytic contact provided that the initial ratio was 100,

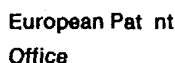
indicating that the catalyst mixture had an outstanding CO reducing effect.

WHAT WE CLAIM IS :

1. A catalyst for use in cleaning particulates in exhaust gases, comprising in combination:
 - (a) at least one component selected from the group consisting of metallic copper and copper compounds;
 - (b) at least one component selected from the group consisting of metallic molybdenum, metallic vanadium, molybdenum compounds and vanadium compounds; and
 - (c) at least one component selected from alkali metal compounds.
2. The catalyst according to claim 1 which further comprises (d) at least one component selected from the group consisting of metallic platinum, metallic palladium, metallic rhodium, platinum compounds, palladium compounds, and rhodium compounds.
3. The catalyst according to claim 1 or 2 wherein the catalyst is further combined with at least one carrier selected from titania, gamma-alumina, and silica-alumina.
4. The catalyst according to claim 1 wherein component (a) comprises copper chloride, copper nitrate and copper oxide.

5. The catalyst according to claim 1 wherein component (b) comprises ammonium salts, chlorides and oxides of molybdenum and vanadium.

6. The catalyst according to claim 1 wherein component (c) comprises compounds of lithium, sodium and potassium.



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EP 83 10 0837

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
Y	US-A-4 298 354 (H.F. HARDMAN) * Abstract; column 3, line 29 - column 5, line 10; claims 1-10 *	1-3, 6	B 01 D 53/36 B 01 J 23/84 B 01 J 23/88 B 01 J 23/89
Y	GB-A-1 058 706 (TEXACO) * Page 1, lines 47-74; page 2, lines 23-62; page 3, lines 13-104; page 4, lines 2-59; claims 1-21 *	1-6	
Y	GB-A-1 068 186 (DU PONT) * Page 1, lines 37-56; page 2, lines 43-95; claims 1-13 *	1	
A	US-A-3 849 336 (LLOYD)		
A	US-A-3 438 721 (B. INNES)		
A	US-A-4 279 777 (VELENYI)		
A	GB-A-1 183 079 (REPUBLIC OF FRANCE)		
A	GB-A-1 438 806 (MITSUBISHI)		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01-08-1983	Examiner LO CONTE C.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 2)
A	US-A-4 304 658 (REINHARD) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 2)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01-08-1983	Examiner LO CONTE C.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			